

FORM PTO-1390 (Modified) (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 213252US0PCT
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 09/926100)
INTERNATIONAL APPLICATION NO. PCT/FR00/00521	INTERNATIONAL FILING DATE 02 MARCH 2000	PRIORITY DATE CLAIMED 03 MARCH 1999	
TITLE OF INVENTION NEUTRON ABSORBENT MATERIAL CONTAINING BORON CARBIDE AND HAFNIUM, AND PROCESS FOR MANUFACTURING THIS MATERIAL			
APPLICANT(S) FOR DO/EO/US Bruno PROVOT, et al.			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below. 4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). 10. <input checked="" type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)). 11. <input type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). 12. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210). <p>Items 13 to 20 below concern document(s) or information included:</p> <ol style="list-style-type: none"> 13. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 15. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 16. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 17. <input type="checkbox"/> A substitute specification. 18. <input type="checkbox"/> A change of power of attorney and/or address letter. 19. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. 20. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 21. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 22. <input type="checkbox"/> Certificate of Mailing by Express Mail 23. <input checked="" type="checkbox"/> Other items or information: <p>Request for Consideration of Documents in International Search Report Notice of Priority / PCT/IB/304 / PCT/IB/308 / Drawings (2 sheets) Amended Sheets (pages 5, 5a, 10, 11, 15, 16, 17, 18, 19, 29, 30 and 31)</p>			

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 09/926100		INTERNATIONAL APPLICATION NO. PCT/FR00/00521		ATTORNEY'S DOCKET NUMBER 213252US0PCT	
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24. The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00 <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY <div style="border: 1px solid black; height: 100px; width: 100%;"></div>	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$130.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	12 - 20 =	0	x \$18.00	\$0.00	
Independent claims	1 - 3 =	0	x \$80.00	\$0.00	
Multiple Dependent Claims (check if applicable) <input type="checkbox"/>				\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$990.00	
<input type="checkbox"/> Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				\$0.00	
SUBTOTAL =				\$990.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				\$0.00	
TOTAL NATIONAL FEE =				\$990.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL FEES ENCLOSED =				\$990.00	
				Amount to be: refunded	\$
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a. ☒ A check in the amount of \$990.00 to cover the above fees is enclosed.


b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

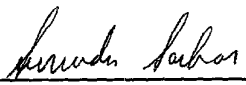
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Norman F. Oblon
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24,618
 REGISTRATION NUMBER
Aug. 31 2001
 DATE

213252US-0 PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :
BRUNO PROVOT ET AL : ATTN: APPLICATION DIVISION
SERIAL NO: NEW US PCT APPLN. :
(BASED ON PCT/FR00/00521)
FILED: HEREWITH :
FOR: NEUTRON ABSORBENT MATERIAL
CONTAINING BORON CARBIDE AND
HAFNIUM, AND PROCESS FOR
MANUFACTURING THIS MATERIAL

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows

IN THE CLAIMS

Please amend the claims as follows:

4. (Amended) Process according to claim 1, in which the grain size of the boron carbide powder ranges up to approximately 50 μm .
5. (Amended) Process according to claim 1, in which the grain size of the hafnium powder ranges up to approximately 20 μm .

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6. (Amended) Process according to claim 1, in which the grain size of the hafnium powder ranges up to approximately 10 μm .

9. (Amended) Process according to claim 1, in which the homogeneous mixture is sintered in a graphite mould lined with a graphite sheet.

10. (Amended) Process according to claim 1, in which the mixture is sintered at a temperature of approximately 1800°C to 2100°C, at a pressure of around 70 to 110MPa for a period of approximately 15 to 90 minutes.

11. (Amended) Process according to claim 1, in which the mixture is sintered at a temperature of approximately 2000°C, at a pressure of around 92 MPa for a period of approximately 1 hour.

12. (Amended) Neutron absorbent material containing boron carbide and hafnium diboride obtained using a process according to claim 1.

REMARKS

Claims 1-12 are active in the present application. The claims are amended to remove multiple dependencies. No new matter is added. An action on the merits and allowance of the claims is solicited.

Respectfully submitted,

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Marked-Up Copy

Serial No: _____

Amendment Filed on: _____

8-31-2001

IN THE CLAIMS

--4. (Amended) Process according to [any of claims 1 to 3] claim 1, in which the grain size of the boron carbide powder ranges up to approximately 50 μm .

5. (Amended) Process according to [any of claims 1 to 4] claim 1, in which the grain size of the hafnium powder ranges up to approximately 20 μm .

6. (Amended) Process according to [any of claims 1 to 4] claim 1, in which the grain size of the hafnium powder ranges up to approximately 10 μm .

9. (Amended) Process according to claim 1 [or 6], in which the homogeneous mixture is sintered in a graphite mould lined with a graphite sheet.

10. (Amended) Process according to [any of the preceding claims] claim 1, in which the mixture is sintered at a temperature of approximately 1800°C to 2100°C, at a pressure of around 70 to 110MPa for a period of approximately 15 to 90 minutes.

11. (Amended) Process according to [any of the preceding claims] claim 1, in which the mixture is sintered at a temperature of approximately 2000°C, at a pressure of around 92 MPa for a period of approximately 1 hour.

12. (Amended) Neutron absorbent material containing boron carbide and hafnium diboride obtained using a process according to [any of claims 1 to 11] claim 1.--

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NEUTRON ABSORBENT MATERIAL CONTAINING BORON CARBIDE AND
HAFNIUM, AND PROCESS FOR MANUFACTURING THIS MATERIAL.

FIELD OF THE INVENTION

The invention relates to a composite neutron absorbent material and to a process for manufacturing this material.

Neutron absorbent materials are neutron absorbers.
5 They find application in the manufacture of control rods for example used to control the reactivity of nuclear reactors, in particular to control pressurized water nuclear reactors (PWR) and fast neutron reactors (FNR).

10 Inside the cores of nuclear reactors, neutron absorbent materials are indispensable components of the control rods. The latter form the command, adjustment and stoppage systems of reactor reactivity.

The materials which make up these control rods
15 contain nuclides able to absorb the neutrons in order to reduce the reactor's neutron flow.

These neutron-absorbing materials may for example be used in the two main types of French nuclear reactors: Pressurized Water Reactors and Fast Neutron
20 reactors.

The first choice that a core designer must face is which neutron-absorbent nuclide to use. It must meet the requirements of anti-reactivity related to the energy rating of the core: type of fuel and fuel
25 assembly, desired neutron flow, nuclear station power,

etc.. Depending upon desired core power, upon the intensity of the neutron flow, it is essential to provide the necessary antireactivity for normal adjustment of this neutron flow or possibly for the emergency stoppage of nuclear fission reactions. During the fission of a heavy nucleus in the core of a nuclear reactor, a few neutrons are released in the free state. If, among these neutrons that are released, some happen to meet a fissile nucleus and cause its fission they in turn generate descendants which themselves may cause the fission of another nucleus and give birth from generation to generation to a chain reaction. It therefore appears important to control the quantity of free neutrons formed in order to prevent the fission reaction from racing out of control and to maintain this fission in a critical state, that is to say in equilibrium.

Therefore the control rods containing the neutron absorbent materials are mobile rods mounted in the core of nuclear reactors such that they can slide between the fuel assemblies, or mounted in a network of fuel pins of an assembly. Control of core fission is made by inserting or withdrawing these rods from the core of the nuclear reactor by sliding them in or out of position.

The absorbent materials may be used to maintain nuclear fission in the critical state, in which case they form piloting rods. They may also be used to ensure quick stoppage of a chain reaction in which case they form safety rods.

Other criteria may be taken into account in the choice of absorbent material. These criteria are:

- good mechanical properties, in particular a Young's modulus that is as low as possible, moderate ultimate stress, good resistance to mechanical damage and more particularly good resistance to crack propagation,

- a reasonable overall cost (raw material and manufacture),

- good chemical and shrinkage resistance to radiation

- optionally, chemical compatibility with the cladding (generally in stainless steel) which may be used to shield the absorbent.

A great amount of research had been conducted on boron carbide B_4C with the sole view to its use as neutron absorber given its high effective neutron capture cross-section. B_4C absorbent material is used in the form of stacks of sintered cylindrical pellets, made from powders.

Although having substantial chemical inertia, B_4C oxides easily on and after $600^\circ C$ in the presence of oxygen. This compound is also sensitive to water corrosion in the primary PWR medium, in particular when radiated by the neutrons or when subjected to neutron radiation. This is one of the reasons why it is generally inserted in stainless steel cladding.

Also, the lifetime of boron carbide never reaches the theoretical limit fixed by boron exhaustion on account of damage to the material caused by the large quantity of helium and lithium formed by neutron

absorption $^{10}\text{B}(\text{n},\alpha)$, Li. Therefore, under the effect of temperature, one fraction of the helium formed diffuses outside the material while the other accumulates therein, causing swelling and micro-fracturing of the material.

In the particular case of fast neutron reactors, the flow of neutrons (energy greater than 1 MeV) penetrates inside all the absorbent material which causes a volume release of heat whereas the surface of the absorbent is directly cooled by sodium. A substantial radial thermal gradient therefore occurs in the material, which may reach several hundred degrees per centimetre. This thermal gradient involves major tangential heat stresses in the material which cause critical radial cracking and complete fragmentation of the absorbent material.

In the particular case of pressurized water reactors, the flow of neutrons (energy less than a few eV) only penetrates the peripheral part of the absorbent material. The swelling described previously therefore only occurs in a peripheral ring of the absorbent. Differential swelling therefore occurs between the circumference and the core of the absorber pellets which causes major radial stresses, critical tangential cracking superimposing itself upon the micro-cracking previously described, and complete fragmentation of the absorbent material.

The combination of swelling, microfracturing and cracking of the material may, under strong radiation, cause a mechanical interaction between the absorbent material and the steel cladding which may lead to

fracture of the cladding which itself is subject to
weakening firstly by fast neutron radiation and
secondly by the diffusion of a certain amount of boron
5 and carbon derived from the absorbent material.

These two modes of critical cracking are
macroscopic crack phenomena with imposed strain.

It is therefore necessary to develop a neutron
absorbent material which may be used in these two types
of reactors.

This material therefore, in addition to the above-
10 mentioned properties of a low Young's modulus and a low
coefficient of thermal expansion, must offer high heat
conductivity, toughness, resistance to crack
propagation and resistance to mechanical damage.

Document EP-A-0 359 683 describes a neutron
15 absorbent pellet and its process of manufacture. It
describes a scarcely absorbent element obtained by
moulding or sintering a mixture of ceramic powders
(B_4C , HfO_2 , Eu_2O_3) and metal (Hf, Eu, Ni, Cr).

Document WO-A-94/28556 describes a neutron
20 absorbent material and its method of preparation. The
material described contains boron carbide and may
contain hafnium, in particular hafnium diboride. The
hafnium diboride represents no more than 40 % by
volume, preferably from 20 to 30 % by volume.

25

DISCLOSURE OF THE INVENTION

The purpose of the present invention is precisely
to remedy the above-mentioned disadvantages and to
provide a neutron absorbent material having all the

ART 34 AMDT

09/926100 09/926100

ART 34 ANDT

English translation of the amended sheets of International
Preliminary Examination

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required properties, in particular for its use in
control rods for a nuclear reactor.

5 The neutron absorbent material of the present
invention is characterized in that it contains boron
carbide and hafnium, in particular it may contain boron
carbide and hafnium diboride.

10 According to the invention, the boron may account
for at least approximately 65% by atoms of the
material, for example approximately 72% by atoms of the
material.

15 According to the invention, the hafnium may
account for up to approximately 18% by atoms of the

material, for example approximately 10% by atoms of the material.

According to the invention, the boron carbide may be in the form of particles having a diameter of up to approximately 50 μm .

According to the invention, the hafnium may be in the form of agglomerates of hafnium boride whose size preferably ranges up to approximately 500 μm , for example up to approximately 250 μm .

The material of the present invention may have a density of approximately 2870 to 6800 kg/m^3 , for example of approximately 3220 to 5770 kg/m^3 , for example of 5165 kg/m^3 or 5060 kg/m^3 .

The material of the present invention may also contain carbon and/or traces of hafnium carbide.

The material of the present invention may also contain zirconium representing up to approximately 4% by weight of the hafnium fraction. The zirconium may be an impurity present in the hafnium, and may represent up to 4% by weight of the hafnium.

The present invention also relates to a control rod for a nuclear reactor containing a neutron absorbent material according to the present invention.

The control rods may be command, adjustment and reactivity stoppage rods for nuclear reactors. The neutron absorbent material of the present invention may, for example, be used in all the above-mentioned applications.

The present invention also concerns a process for manufacturing a neutron absorbent material, said neutron absorbent material being a composite material

containing boron carbide and hafnium diboride. The boron carbide and hafnium diboride may be the main components of the material of the invention.

This process comprises the following steps:

- 5 - adding hafnium powder to a powder of boron carbide,
- mixing the boron carbide powder and the hafnium powder in homogeneous manner, and
- sintering the homogeneous mixture obtained at a
- 10 sintering pressure and temperature that are sufficient to obtain the composite material.

According to the process of the invention, between 15 and 40% by volume of hafnium may be added, for example between 20 and 30% by volume of hafnium, for
15 example around 25% by volume of hafnium. It is also to be noted at this point that the hafnium may contain a weight fraction of zirconium of up to 4% by weight of the hafnium, the zirconium possibly being an impurity usually found in hafnium. The homogeneous mixture of
20 the powders of boron carbide and hafnium, represents 100% by volume of the mixture.

According to the process of the invention, the boron carbide powder may preferably have a grain size of up to approximately 50 μm .

25 According to the process of the invention, the hafnium powder may preferably have a grain size of up to approximately 20 μm , further preferably of up to approximately 10 μm .

30 According to the process of the invention, the mixture of boron carbide powder and hafnium powder may be made using any means known to persons skilled in the

art to obtain a homogeneous mixture of said powders. Preferably, the mixture of these powders may be made by simultaneous application of mechanical stirring and ultrasound, or simply by application of ultrasound to a
5 paste containing said powders dispersed in a dispersion liquid.

The dispersion liquid is preferably a liquid which, after the mixing of the powders, may be easily removed by evaporation for example. This dispersion
10 liquid may, for example, be an alcohol such as ethanol.

When a homogeneous mixture of the powders is obtained, it may be dried by alcohol evaporation for example, and then screened in order to remove any powder aggregates in the mixture.

15 The homogeneous mixture obtained is then sintered to obtain the composite material.

According to the invention, sintering may be conducted in a vacuum or in any atmosphere made up of a neutral gas, preferably argon for example.

20 According to the invention, the mixture may be sintered in any appropriate mould for sintering such powders, for example a mould in graphite preferably lined with a sheet of graphite. Lining of the mould particularly prevents diffusion of the chemical species
25 in the mixture towards the mould and facilitates subsequent release of the composite material from the mould.

The mould may be of appropriate shape to mould the material in pellet, plate, cruciform or pin shape and
30 generally in a shape appropriate for forming control rods of a nuclear reactor.

Sintering of the mixture is advantageously conducted under conditions of temperature, pressure and time which enable proper densification of the composite material, it may for example be conducted at a
5 temperature of approximately 1800 to 2100°C, for example at a temperature of around 2000°C, under a pressure of 70 to 110 MPa, for example from 90 to 100 MPa, for example of around 92 MPa, for a time of approximately 15 to 90 minutes, for example for
10 approximately 1 hour.

Sintering may, for example, be conducted in a furnace maintained in a dynamic vacuum.

Sintering pressure may be applied before the reaction which occurs in the mixture of the boron
15 carbide and hafnium powders. Therefore, the pressure may be applied before the temperature of the powder mixture reaches the sintering reaction temperature of said mixture, for example when the temperature of the mixture and the mould is approximately 20 to 1200°C,
20 for example around 500 to 1000°C, or further at approximately 800°C for example.

Under these conditions, reactive sintering in the powder mixture, thermal contact between the boron carbide and hafnium powders and the composition, and
25 the morphology of the composite material are accurate. In addition, the densification of the composite material of the present invention is most satisfactory.

One first advantage of the neutron absorbent material of the invention is that it offers greater
30 resistance to crack propagation.

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Preliminary Examination Report

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Another advantage of the material of the invention is that it maintains its geometrical intactness despite major mechanical damage. For the composite material of the invention does not fragment when subjected to a strong heat gradient, swelling,
5 microfracturing or cracking.

A further advantage according to the invention was demonstrated by biaxial bending tests performed on sample disks of pure boron carbide material. These tests showed that the fracture behaviour of pure boron
10 carbide was solely fragile, leading to fragmentation of the material. With the composite material of the invention, fracture behaviour is pseudo-plastic and dissipating: it does not lead to fragmentation of the composite material of the invention which, after
15 mechanical damage, remains in a single block even if microfractured or cracked. This result indicates a Young's modulus of the composite material of the present invention that is lower than that of pure boron carbide, to an elongation to fracture of the composite
20 material of the present invention that is greater than that of pure boron carbide, and to a Weibull's modulus of the composite material of the present invention that is greater than that of pure boron carbide, and hence indicates lesser dispersion of fracture probability in
25 relation to a given stress which may occur in the material.

Another advantage of the invention was shown by comparative double-torsion tests on sample plates of pure boron carbide and a material of the invention.
30 These tests showed pure boron carbide to have solely

ART 34 AMDT

English translation of the amended sheets of International
Preliminary Examination Report

11

fragile crack behaviour with intragranular cracking. For the composite material of the invention, crack behaviour showed phenomena of repeated crack blocking, phenomena of crack deflection, and crack bridging
5 phenomena in the composite structure of the material of the invention. The result was resistance to crack propagation and toughness of the composition material of the present invention that was greater than that of pure boron carbide. This result also shows an R curve
10 effect exhibited by the composite material of the present invention through the double torsion test.

A further advantage of the invention was shown by heat gradient cracking tests on sample disks of pure boron carbide and sample disks of the material of the
15 present invention. These tests showed solely fragile cracking and instantaneous intragranular cracking with the pure boron carbide material. Pure boron carbide cannot withstand a heat gradient representing the heat gradient which occurs under radiation in a fast neutron
20 reactor. This is due to the thermo-mechanical stresses induced by the heat gradient which exceed the crack propagation resistance of pure boron carbide and causes fragmentation of the sample of pure boron carbide. With the composite material of the present invention, cracks also occurred in the sample disks but
25 they were blocked by the structure of the material of the invention. The sample disks of the composite material of the present invention remained in a single piece. The cracks were shorter as their growth was blocked by the presence of agglomerates of hafnium boride which limited their
30 propagation. This result is the effect of the heat

conductivity, resistance to crack propagation and toughness of the composite material of the present invention which are greater than those of pure boron carbide, and of an R curve effect exhibited by the composite material of the present invention with the double-torsion test.

The composite absorbent material of the invention may, for example, be described as containing a homogeneous matrix of boron carbide (B_4C) in which agglomerates are distributed in homogeneous manner which contain hafnium monoboride (HfB), hafnium diboride (HfB_2) and traces of hafnium carbide (HfC). Zones of free carbon (C) can be detected on the interface between the matrix and the agglomerates, preferably this free carbon phase does not exceed 10% by weight of the boron carbide phase. The added hafnium therefore develops into hafnium boride phases present in the composite in the form of agglomerates.

The hafnium boride also offers the advantage of having very satisfactory reaction to neutron radiation which is better than that of boron carbide in terms of accommodation of strain, radiation defects and microfracturing.

The type of the agglomerate phases during reactive sintering may therefore be of importance in understanding the advantage of the composite material of the invention.

The phases of hafnium boride in the composition of the present invention have the appearance of agglomerates. These agglomerates in the composite material of the invention provide the composite

material with the capacity to resist against crack propagation and to maintain its physical intactness despite the slow, progressive lowering of its mechanical characteristics.

5 Other characteristics and advantages will be further seen on reading the following examples which are evidently given for illustrative purposes and are not restrictive, with reference to the appended figures.

10

DESCRIPTION OF THE FIGURES

- figure 1 is a graphical representation of the influence of the sinter cycle on the sintering temperature of a mixture of B_4C and Hf powders
15 according to the present invention,

- figure 2 is a graphical representation of the fracture behaviour of pure boron carbide and of a material of the present invention in the case in example 1,

20 - figure 3 is a graphical representation of the crack behaviour of pure boron carbide and of a composite B_4C/Hf material according to the present invention in the case described in example 1,

25 - figure 4 is a graphical representation of the R-curve effect observed in the composite B_4C/Hf material of the present invention in the case described in example 1.

Example 1: Manufacture of a composite material
30 according to the invention.

18.9 g of boron carbide powder having an average grain size of less than 50 μm were mixed with 32.75 g of hafnium having an average grain size of less than 20 μm , that is 75 % by volume of boron carbide and 25 % by volume of hafnium.

The mixture was made as homogeneous as possible through the application of ultrasound to a paste made of the two powders dispersed in ethanol.

The mixture was then dried in a drying oven heated to 80°C, then screened with a screen of 60-micron mesh size. 2.5 g of this mixture were placed in a graphite mould 9.5 mm in diameter. Two pistons in graphite plugged the end of the mould previously lined with a sheet of graphite having a thickness of 0.5 mm and allowing pressure to be applied to the powder.

The mixture and mould assembly were brought to 2000°C under a pressure of 92 MPa for one hour in a furnace maintained in a dynamic vacuum. The pressure of 92 MPa was applied when the temperature of the mould and mixture assembly reached 800°C and it was maintained for the duration of the temperature rise and throughout the one hour stage. Pellets of 8.5 mm in diameter were obtained and 8.5 mm in height after machining with a diamond tool. The pellets showed a final density of 98% of theoretical density, that is a density of 5060 kg/m³.

Example 2: Application of pressure at low temperature to obtain the composite of the invention.

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Preliminary Examination Report

15

Under the same conditions as in example 1, different mixtures of boron carbide and hafnium powders were sintered with different sintering cycles.

The sintering cycle may be defined by a certain
5 number of parameters:

- sintering temperature: this is the maximum temperature reached during sintering, chosen to obtain the density, the composition and the morphology of the composite of the invention,

10 - sintering time: the time during which the mixture is maintained at sintering temperature,

- sintering pressure: the pressure applied to the mixture during the sintering time,

- pressurizing temperature of the mixture; the
15 temperature at which the pressure is applied to the mixture.

For each of these sintering operations, the density of the composite material obtained was measured and its composition successively identified by X-ray
20 diffraction after sintering the composite.

For each mixture a relative density (rd) was measured as a percentage of the composite material obtained after sintering, by calculating the ratio of the measured density and the theoretical density after
25 sintering.

Table 1 below groups together the results of this example.

30

English translation of the amended sheets of International
Preliminary Examination Report

16

Table 1

Sintering temperature in °C		1000	1200	1300	1400	1800	1900	2000
Pressurizing at sinter temperature and sintering pressure of 60 MPa	rd as %	58	60	61	-	67	-	70
Pressurizing at sinter temperature and sintering pressure of 110 MPa	rd as %	-	65	-	68	-	80	83
Pressurizing at 800°C and sintering pressure of 92 MPa	rd as %	-	68	69	-	85	-	99

In figure 1, the values of figure 1 are plotted to form a relative density graph as a % of composite material relative to sintering temperature, with 60 MPa sinter pressure applied at sinter temperature: curve denoted 2, with 110 MPa sinter pressure applied at sinter temperature: curve denoted 4, and finally with low temperature pressurization at 800°C with a sinter pressure of 92 MPa: curve denoted 6.

This figure shows the influence of the sinter cycle parameters and of sintering temperature on a mixture of boron carbide and hafnium according to the invention.

The results of this example generally show that the temperature at which pressure is applied the mixture may be essential to obtain the composite of the invention having relative densities varying between 80 and 99% of the theoretical density of the initial mixture after reactive sintering.

Different composite materials of the invention were analysed by X-ray diffraction. These composite materials were obtained with pressurization at low temperature and a sintering pressure of 92 MPa for increasing sinter temperatures: 1000°C, 1200°C, 1400°C,

English translation of the amended sheets of International
Preliminary Examination Report

17

1800°C, 1900°C and 2000°C. Analysis of X-ray diffraction spectra made it possible to follow the changes in the chemical composition of the composite of the invention in relation to sintering temperature.

- 5 With this analysis, the different phases present in the composite of the invention could be identified in order to obtain the most favourable chemical composition for improved performance under neutron radiation.

The results are summarized in table 2 below:

10

Table 2

Sinter temperature in °C	Type of phases present in the composite material of the invention
1000	Boron carbide B ₄ C Hafnium Hf Hafnium monoboride HfB Hafnium carbide HfC Hafnium diboride HfB ₂
1200	Boron carbide B ₄ C Hafnium Hf Hafnium diboride HfB ₂ Hafnium monoboride HfB Hafnium carbide HfC Carbon C
1400	Boron carbide B ₄ C Hafnium diboride HfB ₂ Hafnium monoboride HfB Hafnium Hf Hafnium carbide HfC Carbon C
1800	Boron carbide B ₄ C Hafnium diboride HfB ₂ Hafnium monoboride HfB Carbon C traces: Hafnium Hf Hafnium carbide HfC
1900	Boron carbide B ₄ C Hafnium diboride HfB ₂ Carbon C traces: Hafnium monoboride HfB

English translation of the amended sheets of International
Preliminary Examination Report

18

2000	Boron carbide B_4C Hafnium diboride HfB_2 Carbon C
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These results generally show that, at the outset, when the conditions of thermal contact between the two boron carbide and hafnium phases in the initial mixture of powders are in accordance with those of the present invention, a set of chemical reactions occurs during sintering which involves changes in the chemical composition of the material of the invention.

A further effect of the mode of sintering the composite material of the invention is the structure which forms during sintering. It is in the form of a matrix of boron carbide and agglomerates of a hafnium boride phase which imparts improved heat conductivity to the material and improved fracture and crack behaviour as described in particular in examples 3 and 4 below.

Example 3: Evaluation of the resistance to mechanical damage of a composite material according to the invention.

Ultimate stress is the macroscopic magnitude characterizing the yield strength of a material. It is the critical value of the maximum stress calculated on a test-piece of the material under consideration. This ultimate stress is related to critical defects involved

English translation of the amended sheets of International
Preliminary Examination Report

19

in the yield of the structure according to Griffith's theory.

Elongation to fracture is the macroscopic magnitude which represents the elongation or strain of
5 a test-piece when fracture of the latter occurs, that is to say when the ultimate stress is reached.

Young's modulus is the macroscopic magnitude characterizing the elasticity of a homogeneous, isotropic material. When characterizing a material,
10 Young's modulus of the material is the ratio of the stress calculated in the material to corresponding strain. Young's modulus is also the sloping straight line representing stress evolution calculated in a sample and the measured corresponding strain.

15 The biaxial bending test chosen in our case was used to test a material under planar stress whose test-pieces are in the form of disks of narrow thickness (thin plate theory). Load is transmitted via a central bead (point contact) on the upper surface of the test-
20 piece of the material to be tested. With this configuration, it is possible to obtain an axisymmetrical area of uniform stresses at the centre of the test-piece of material to be tested. The test-piece is supported by three beads distributed around a
25 circle whose centre is positioned in the extension of the load line. The test has the advantages of easy, reliable test-piece preparation, low experimental dispersion of measurements (reduced edge effects and uniform load area) and of material testing in biaxial
30 mode.

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This test is used to measure the load placed on the test-piece and its deflection during the test. During biaxial bending under load of the test-piece, the continuous recording of the variation in deflection relative to the load applied is used to assess Young's modulus throughout the elastic regimen. When the load reaches a sufficient critical value to cause breakage of the test-piece, this critical load is used to calculate the ultimate stress of the material, and the deflection is used to determine the elongation or strain to fracture (elongation or strain corresponding to the time of fracture).

The material in pure boron carbide is solely elastic: Young's modulus is a constant which suffices to describe the entire curve representing stress evolution relative to strain up to the time of fracture; for this material, the curve is a simple, monotonous, continuous straight line.

It is also fragile: fracture occurs instantly and leads to the collapse of all the characteristics of the material (Young's modulus and ultimate stress), it is no longer possible to apply a load to this material since it no longer offers any mechanical resistance. The curve representing deflection relative to load (or of load relative to deflection) is a monotonous, continuous straight line which suddenly ends at the time of fracture of the test-piece. The elastic energy stored during loading of the test-piece is suddenly returned on breaking, and leads to fragmentation of the test-piece.

On the other hand, the performance of the material of the present invention is pseudo-plastic: Young's modulus is no longer sufficient to describe the entire curve representing stress evolution relative to strain which is not a simple straight line.

Moreover, it is dissipative: despite the damage which occurs in the material of the present invention, it is still possible to apply a load to the test-piece which maintains mechanical resistance. The elastic energy stored is gradually dissipated with the onset of damage in the test-piece. The curve representing load evolution relative to deflection is not a simple, monotonous straight line which suddenly ends, but it shows a slow, progressive decrease in load relative to deflection. This performance conveys slow, progressive decrease in the mechanical resistance of the material and a progressive decrease in the mechanical characteristics of the material: Young's modulus and ultimate stress. In addition, the fracture of the composite material of the present invention no longer involves its fragmentation, and it remains in a single piece showing cohesive behaviour.

Table 3 below groups together the mechanical characteristics obtained with biaxial bending tests using one same test-piece geometry both for pure boron carbide and for the material of the present invention in the case described in example 1, and table 4 below groups together the results of the biaxial bending tests with pure boron carbide and with the material of the present invention.

Table 3: Mechanical characteristics of the material

	Young's modulus 10^9 Pa	Ultimate stress 10^6 Pa	Elongation to fracture 10^{-6} Pa
B ₄ C	360	400	50
B ₄ C + 25% vHf (example 1)	250	200	250

Figure 2 gives the results obtained so as to represent the changes in load applied to the test-piece in Newtons relative to the corresponding deflection expressed in microns up until total destruction of the test material for pure boron carbide: curve denoted 8, and for the material of the present invention: curve denoted 10. This figure shows the difference in fracture behaviour between pure boron carbide and the material of the present invention.

Curve 8 in particular shows the solely fragile behaviour of pure boron carbide. Curve 10 shows the pseudo-plastic, dissipative behaviour of the B₄C/Hf composite of the present invention.

Lowering of Young's modulus leads to lowering of the stresses undergone by the material subjected to imposed strain and therefore less demand is placed on the material in the event of degradation as set forth in the paragraph of the prior art.

Lowering of ultimate stress makes it possible to store less elastic energy during normal functioning of the material before breakage, and therefore the early onset of non-critical micro-cracks allows gradual dissipation of this mechanical energy without causing fragmentation of the material.

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The substantial increase in elongation to rupture of the composite material of the present invention is a consequence of the first two changes in the mechanical properties of the material. The composite material is able to degrade slowly and progressively while maintaining very suitable mechanical integrity. Consequently, the composite material of the invention may undergo up to around tenfold more strain than a material of the prior art before it no longer shows any mechanical resistance. Even at this stage of severe degradation, the composite material of the invention, which no longer has any mechanical resistance, still remains in a single piece without fragmenting.

The B_4C /Hf composite of the invention therefore shows better fracture behaviour than pure boron carbide.

Example 4: Evaluation of crack propagation resistance in a material of the invention.

Toughness is the macroscopic magnitude characterizing a material's resistance to crack propagation. It is the critical value of the stress intensity factor calculated at a pre-crack made in the material under consideration. This pre-crack creates a critical defect of much greater size than that of any other defects naturally existing in the test-piece.

The double-torsion test chosen in our case consists of making a 3 mm cut in a rectangular plate (length 35 mm x width 17 mm x thickness 2 mm) and of tapering the tip of this cut by successive Knoop indentations along the median axis the length of the

test-piece. The characteristics of the defect made must be as close as possible to those of a natural defect, in particular the curvature radius at the bottom of the cut must be very low. The crack is initiated under the point of application of the load starting from the pre-crack and extending along the axis of the test-piece.

The test consists of bending three points at the tip of the plate, of opening the crack to cause its propagation, controlling the applied stress and recording displacement under the tip of the cut. The plate is supported on four point rests, and the load is transmitted via another point rest at the tip of the pre-crack.

Test procedure consists of applying a bending force to the test-piece which increases at a constant rate (5 $\mu\text{m}/\text{min}$).

Measurement of the critical load P_c causing propagation of the crack is used to calculate toughness.

If the material so permits, blockages may occur during propagation of the crack after it has started to grow, that is to say if the previously defined toughness is exceeded at one point of the material.

Also, if the material so permits, local strengthening phenomena may occur vis-à-vis crack propagation. These phenomena indicate an increase in apparent toughness relative to the position of the tip of the crack at the time the crack starts to grow again when local toughness has been overcome. Therefore with the above-described double-torsion test, it is possible to plot a graph showing the evolution of apparent

toughness calculated for each successive re-growth of the crack relative to the length of the crack developing in the double torsion test-piece.

5 The effect which involves an increase in apparent toughness relative to the length of the crack propagating in the material is called the R-curve effect, that is to say the ability of the material to resist crack propagation as and when a crack propagates. This R-curve effect may be identified by
10 the previously described graph showing the development of toughness relative to the length of the crack.

Figure 3 gives the curves obtained during double-torsion tests showing the changes in load applied to the test-piece in Newtons relative to the corresponding
15 deflection measured in microns up until total propagation of the crack in the test material for pure boron carbide: curve denoted 12, and for the material of the present invention: curve denoted 14. This figure shows the difference in crack behaviour between pure
20 boron and the material of the present invention.

In particular, curve 14 exhibits the successive phenomena of crack blockage, expressing local strengthening in the B_4C /Hf composite of the present invention. After blockage of the crack expressed by
25 relaxing of the applied load, if crack propagation is to continue the applied load must be increased to cause further growth of the crack.

Curve 12 displays the instantaneous cracking of the material in pure boron carbide with no
30 strengthening phenomena.

Figure 4 shows curve 16 representing the development in apparent toughness of the composite material of the invention relative to the length of the crack which propagates in a double torsion test-piece. This bell-shaped curve demonstrates the R-curve effect which exists in the crack behaviour of the B₄C/Hf composite of the present invention.

The increase in resistance to crack propagation of the composite material of the invention is in the order of 40% (increase in the resistance to crack propagation from 3.5 to 4.9 Mpa.m^{1/2}), when the crack propagates between $\frac{1}{4}$ and $\frac{3}{4}$ of test-piece length. When the length of the crack is too great relative to the length of the double-torsion test-piece (34 mm), resistance to crack propagation is reduced. This reduction corresponds to final destruction of the material.

The following table is a discrete representation of curve 16 shown in figure 4.

Table 4

Crack length in mm	Apparent toughness in Mpa.m ^{1/2}
8.0	3.5
9.0	3.7
12.2	4.3
13.9	4.4
17.5	4.6
20.7	4.8
23.0	4.8
23.2	4.9
23.7	4.9
25.2	4.4
25.2	4.3

25.5	4.1
------	-----

Micrograph analysis shows the difference in fracture and crack behaviour firstly of pure boron carbide and secondly of the composite material of the invention.

In particular, it shows the fragmentation of the pure boron carbide, whereas despite the propagation of cracks in the composite material of the present invention, the latter remains in a single piece and is not fragmented.

Table 5 below shows the measurements made by the double-torsion test of the toughness of pure boron carbide and of the composite material B_4C/Hf according to the invention in the case of example 1.

Table 5: Material toughness

Materials	KIC toughness $10^6 \text{ Pa.m}^{0.5}$
Boron carbide B_4C	3.5
$\text{B}_4\text{C}/\text{Hf}$ composite	5.0

5 The $\text{B}_4\text{C}/\text{Hf}$ composite of the invention shows resistance to crack propagation which increases as the cracks propagate. The crack behaviour of the $\text{B}_4\text{C}/\text{Hf}$ composite of the present invention therefore shows an R-curve effect.

10 The $\text{B}_4\text{C}/\text{Hf}$ composite of the invention exhibits greater toughness than the toughness of pure boron carbide.

The $\text{B}_4\text{C}/\text{Hf}$ composite of the invention therefore displays better crack behaviour than pure boron carbide.

1. Process for manufacturing a neutron absorbent material, said material being a composite material containing boron carbide and hafnium, comprising the
5 following steps:

- adding hafnium powder to a powder of boron carbide,
- mixing the boron carbide powder and the hafnium powder such as to obtain a homogeneous mixture, and
10 - sintering the homogeneous mixture at sufficient sintering pressure and temperature to obtain a composite material, characterized in that the sintering pressure is applied before the temperature of the homogeneous mixture of
15 the powders reaches the sinter reaction temperature of said mixture.

2. Process according to claim 1, in which up to approximately 40% by volume of hafnium is added, the
20 homogeneous mixture of the boron carbide and hafnium powders representing 100% by volume.

3. Process according to claim 1, in which approximately 25% by volume of hafnium is added, the
25 homogeneous mixture of the boron carbide and hafnium powders representing 100% by volume.

4. Process according to any of claims 1 to 3, in which the grain size of the boron carbide powder ranges
30 up to approximately 50 μm .

5. Process according to any of claims 1 to 4, in which the grain size of the hafnium powder ranges up to approximately 20 μm .

5

6. Process according to any of claims 1 to 4, in which the grain size of the hafnium powder ranges up to approximately 10 μm .

10

7. Process according to claim 1, in which the mixture of boron carbide and hafnium powders is made by applying ultrasound to a paste containing said powders dispersed in a dispersion liquid.

15

8. Process according to claim 1, in which the homogeneous mixture is sintered in a vacuum or in an atmosphere formed of a neutral gas.

20

9. Process according to claim 1 or 6, in which the homogeneous mixture is sintered in a graphite mould lined with a graphite sheet.

25

10. Process according to any of the preceding claims, in which the mixture is sintered at a temperature of approximately 1800°C to 2100°C, at a pressure of around 70 to 110MPa for a period of approximately 15 to 90 minutes.

11. Process according to any of the preceding claims, in which the mixture is sintered at a

ART 34 ANDT

English translation of the amended sheets of International
Preliminary Examination Report.

31

temperature of approximately 2000°C, at a pressure of around 92 MPa for a period of approximately 1 hour.

12. Neutron absorbent material containing boron carbide and hafnium diboride obtained using a process according to any of claims 1 to 11.

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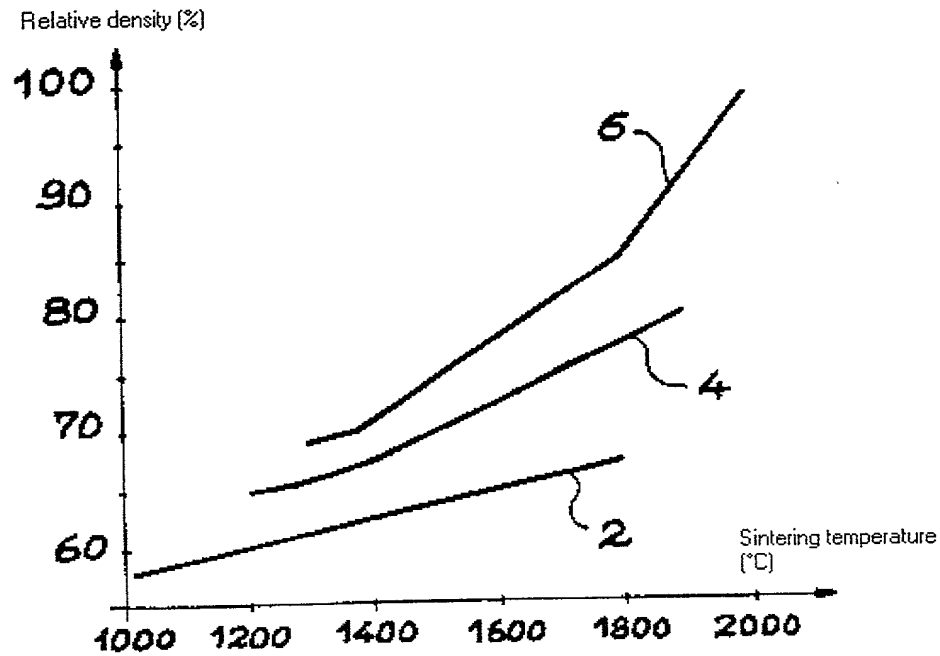


FIG. 1

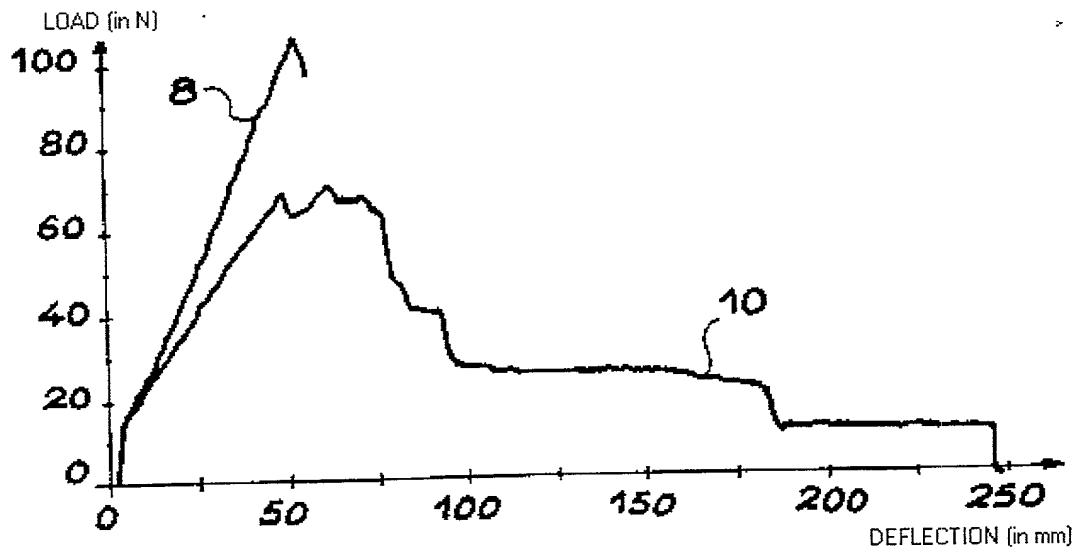


FIG. 2

2 / 2

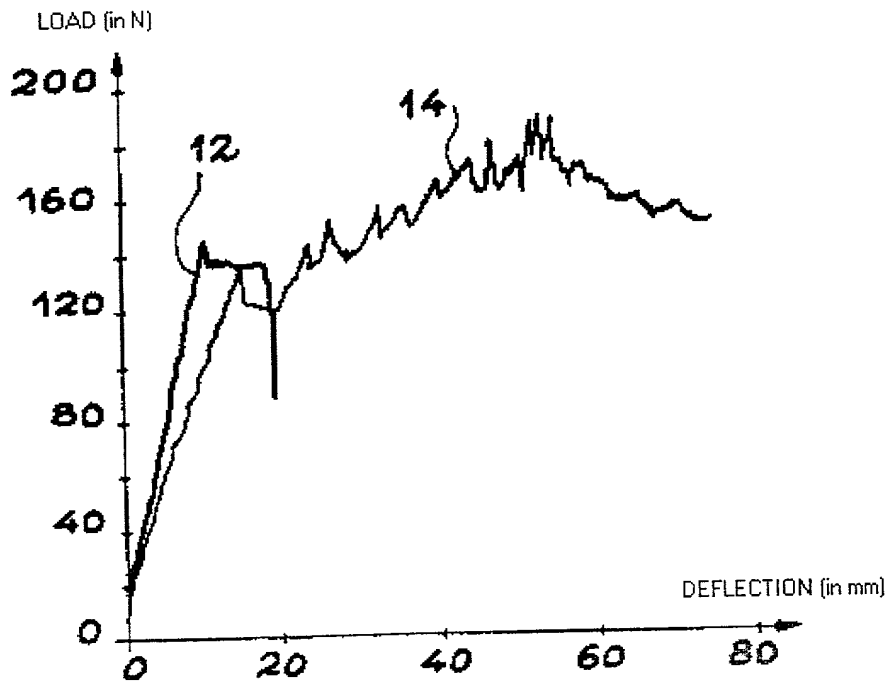


FIG. 3

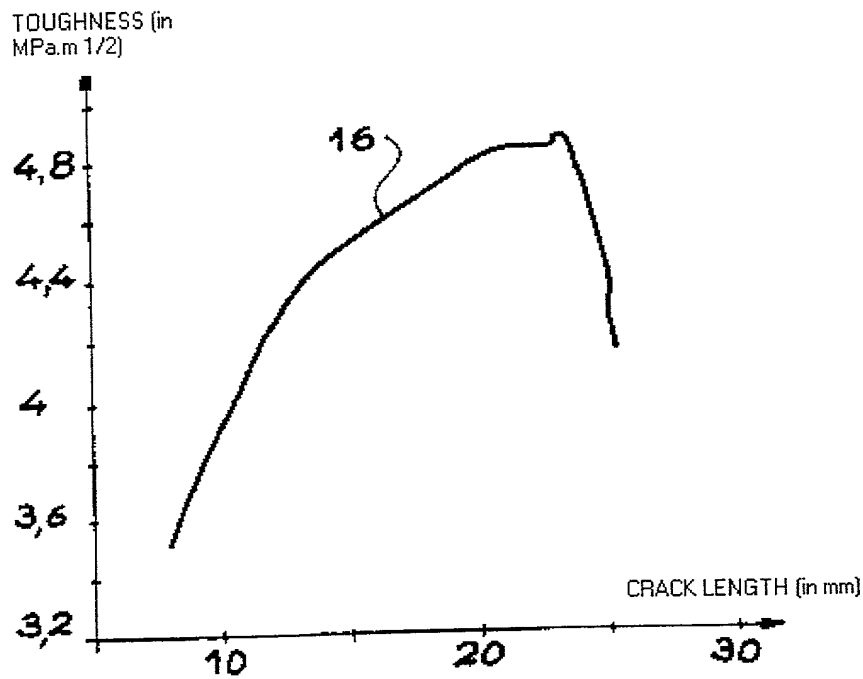


FIG. 4

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Declaration, Power Of Attorney and Petition

Page 1 of 3

WE (I) the undersigned inventor(s), hereby declare(s) that :

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled :

NEUTRON ABSORBENT MATERIAL CONTAINING BORON CARBIDE AND HAFNIUM, AND PROCESS FOR MANUFACTURING THIS MATERIAL.

the specification of which

☐ is attached hereto.

☐ was filed on

as Application Serial No.

and amended on

☒ was filed as PCT international application

Number PCT/FR00/00521

on March 02, 2000

and was amended under PCT Article 19

on May 03, 2001 and May 15, 2001

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119 (a)-(d) or § 365 (b) of any foreign application(s) for patent or inventor's certificate, or § 365 (a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application (s)

Application No.	Country	Day/month/Year	Priority Claimed
99 02631	FRANCE	03 MARCH 1999	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
_____	_____	_____	<input type="checkbox"/> YES <input type="checkbox"/> NO
_____	_____	_____	<input type="checkbox"/> YES <input type="checkbox"/> NO
_____	_____	_____	<input type="checkbox"/> YES <input type="checkbox"/> NO

We (I) hereby claim the benefit under Title 35, United States Code, § 119 (e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. §120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of prior application and the national or PCT International filing date of this application.

Application Serial No.

Filing Date

Status (pending, patented,
abandoned)

And we (I) hereby appoint : Norman F. Oblon, Registration Number 24,618; Marvin J. Spivak, Registration Number 24,913; C. Irvin McClelland, Registration Number 21,124; Gregory J. Maier, Registration Number 25,599; Arthur I. Neustadt, Registration Number 24,854; Richard D. Kelly, Registration Number 27,757; James D. Hamilton, Registration Number 28,421; Eckhard H. Kuesters, Registration Number 28,870; Robert T. Pous, Registration Number 29,099; Charles L. Gholz, Registration Number 26,395; William E. Beaumont, Registration Number 30,996; Jean-Paul Lavallée, Registration Number 31,451; Stephen G. Baxter, Registration Number 32,884; Richard L. Treanor, Registration Number 36,379; Steven P. Weithroch, Registration Number 32,829; John T. Goolkasian, Registration Number 26,142; Richard L. Chinn, Registration Number 34,305; Steven E. Lipman, Registration Number 30,011; Carl E. Schlier, Registration Number 34,426; James J. Kulbaski, Registration Number 34,648; Richard A. Neifeld, Registration Number 35,299; J. Derek Mason, Registration Number 35,270; Surinder Sachar, Registration Number 34,423; Christina M. Gadiano, Registration Number 37,628; Jeffrey B. McIntyre, Registration Number 36,867; William T. Enos, Registration Number 33,128; Michael B. McKabe Jr., Registration Number 37,182; Bradley D. Lytle, Registration Number 40,073 and Michael R. Casey, Registration Number 40,294 ; our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P.C., whose post Office Address is : Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true ; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardise the validity of the application or any patent issuing thereon.

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